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13. ABSTRACT
To study transport phenomena and electrostatic interactions in negatively charged poly(N-isopropylacrylacrylamide-*co*-acrylic acid) hydrogels, NIPA-AA, electroanalytical experiments with two positively charged probes, ferrocenylmethyltrimethylammonium, $FcTMA^+$, and hexaammineruthenium(III), $Ru(NH_3)_6^{3+}$, cations were performed, and the results compared with those for an uncharged electroactive probe, 1,1'-ferrocenedimethanol, $Fc(MeOH)_2$. Steady-state voltammetry and chronoamperometry at platinum disk microelectrodes were used to determine diffusion coefficients of those probes. For temperatures below the volume phase transition of a gel, there are not significant differences in the transport behavior of cationic and uncharged probes. After the volume phase transition occurs and the gel collapses, the diffusion coefficients of all probes decrease, the change in diffusion coefficient is more pronounced for cationic probes than for a neutral probe, and depends on the charge of the cationic probe. Changes in concentration of cationic species in collapsed NIPA-AA gels were detected as a result of the volume phase transition.

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Transport of Ions and Electrostatic Interactions in Thermoresponsive Poly(N-Isopropylacrylamide-*co*-Acrylic Acid) Hydrogels: Electroanalytical Studies

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ABSTRACT

Poly(N-isopropylacrylacrylamide-*co*-acrylic acid) hydrogels, NIPA-AA, undergo discontinuous reversible volume phase transitions as a response to temperature increase. Those hydrogels are weakly negatively charged and therefore, are expected to interact electrostatically with charged species dissolved in those systems. To study transport phenomena and electrostatic interactions in NIPA-AA hydrogels, electroanalytical experiments with two positively charged probes, ferrocenylmethyltrimethylammonium, $FcTMA^+$, and hexaammineruthenium(III), $Ru(NH_3)_6^{3+}$, cations were performed, and the results compared with those for an uncharged electroactive probe, 1,1'-ferrocenedimethanol, $Fc(MeOH)_2$. Steady-state voltammetry and chronoamperometry at platinum disk microelectrodes were used to determine diffusion coefficients of those probes. For temperatures below the volume phase transition of a gel, there are not significant differences in the transport behavior of cationic and uncharged probes. After the volume phase transition occurs and the gel collapses, the diffusion coefficients of all probes decrease, the change in diffusion coefficient is more pronounced for cationic probes than for a neutral probe, and depends on the charge of the cationic probe. In addition to changes of transport of cationic species in collapsed NIPA-AA hydrogels, changes in their concentration were detected as a result of the volume phase transition.

INTRODUCTION

Discontinuous volume phase transitions are phenomena found in some polymeric gels, which reversibly swell or shrink in volume by as much as several hundred times in response to changes in temperature, pH, ionic strength, electric or magnetic field, or light [1-4]. Phase transition of a polymeric gel is a result of a competitive balance between repulsive forces (the electrostatic interaction between the polymer charges of the same kind, which can be imposed upon a gel by introducing ionization into the network) that act to expand the polymer network, and attractive forces (van der Waals, hydrophobic interactions and hydrogen bonding) that act to shrink the network. The number of applications of stimuli-responsive polymeric gels increases continuously [5]. In addition to medical and biotechnological applications [1], phase transition phenomenon might be very important for gel-based chemical sensors [6] and as electrolytes for batteries and other power sources. Unique properties of these materials have triggered an effort to develop gel-based actuators, sensors, controlled-release drug delivery systems, chemical memories and artificial muscles. To our knowledge, there are no data on transport of ions in polymeric gels that undergo discontinuous volume phase transitions. This knowledge is of great importance for many applications of stimuli-responsive polymeric gels. The diffusion coefficients of neutral probes, such as H_2O, ethanol, glycerin, sucrose, $Fc(MeOH)_2$, and 4-hydroxy-tempo (TEMPO), in swollen thermoresponsive gels have been reported by several groups [7,8]. The relation between the diffusion coefficient of probes and the polymer concentration in gels was discussed using several models, such as scaling theory [7] and obstruction theory [8]. The necessary parameters for these models, such as friction coefficient of the polymeric network in the gel, were measured and reported [9].

Hydrogels consisting of a copolymer of N-isopropylacrylacrylamide (NIPA) and acrylic acid (AA) undergo a discontinuous volume phase transition as a response to temperature changes. They

reversibly swell at lower temperatures and collapse at higher temperatures. The temperature of the volume phase transition depends on the composition of the copolymer and on the composition of the solvent. The earliest systematic study on the volume phase transition of poly(N-isopropylacrylacrylamide-co-acrylic acid) gels, NIPA-AA, were reported by Tanaka et al. [10], and were followed by others [11-14]. We have reported on the preparation and characterization of NIPA-AA hydrogels and gels swollen by methanol, and have investigated transport of molecules in those materials using electroanalytical techniques [8,15,16].

Many experimental techniques have been used to study transport in polymeric gels, including light scattering spectroscopy [17-19], NMR spectroscopy [20-22], radioactive tracer methods [23], as well as electroanalytical techniques, steady-state voltammetry [24] and chronoamperometry [25]. We have shown the effectiveness of steady-state voltammetry in transport studies in NIPA-AA thermoresponsive gels [8,15,16]. The diffusion coefficient, D, of an electroactive probe can be determined from the diffusion-limited steady-state current, i_s, at a disk microelectrode [26] according to the following equation

$$D = i_s / 4nFCr_d \qquad (1)$$

where C is the concentration of an electroactive ion or molecule, r_d is the radius of the microelectrode, n is the number of electrons transferred, F is the Faraday constant. Microelectrodes yield steady-state current on time scales of seconds and make measurements possible in resistive media, such as media with low or no supporting electrolyte. Additionally, the steady-state current at microelectrodes is directly proportional to the flux of a reactant, and therefore, the currents are very sensitive to changes of the diffusion coefficient. However, since steady state voltammetric currents also depend on the concentration of the electroactive probes, the diffusion coefficient can not be determined without knowledge of the concentration of an electroactive species, and it is not possible

to determine both concentration and the diffusion coefficient simultaneously from steady-state voltammetry.

When thermoresponsive hydrogels undergo discontinuous volume phase transition as a response to changes of temperature a fraction of the solvent is expelled from the gel, and two phases are formed, a collapsed gel phase and the expelled solvent/solution phase. As a result of this process, the concentration of species in both phases may differ. Kawasaki et al. [27] studied partition of salts between poly(N-isopropylacrylamide), NIPA, gels and aqueous solutions during volume phase transition of NIPA gels. He found that salts such as LiCl, KCl, KSCN, and CH_3COOLi are excluded from the collapsed gel phase after volume phase transition, and the exclusion tendency depends on the identity of the ions. No results on the distribution of neutral and ionic probes in the NIPA-AA gels or other hydrogels have been reported. Therefore, to study transport and a distribution of species in polymeric gels undergoing discontinuous volume phase transition, a methodology for determination of the diffusion coefficient independent of concentration is required.

Normalized chronoamperometry with disk microelectrodes can be used to determine diffusion coefficient, D, independently of n and C [28,29]. The chronoamperometric transient current, i(t), normalized with the steady-state current, i_s, is given by the following equation [28]

$$i(t)/i_s = 1 + (2/\pi^{3/2})r(Dt)^{-1/2} \qquad (2)$$

and the diffusion coefficient can be determined from the slope of the linear dependence of $i(t)/i_s$ on $t^{-1/2}$. Then the concentration of electroactive species can be calculated from the steady-state current according to eq. 1.

In this paper, we report on electroanalytical studies of transport of ions in thermoresponsive NIPA-AA hydrogels. Since the NIPA-AA polymeric network is weakly negatively charged, we

expect attractive electrostatic interactions with cations. Therefore, we selected two electroactive cationic probes, ferrocenylmethyltrimethylammonium, $FcTMA^+$, and hexaammineruthenium(III), $Ru(NH_3)_6^{3+}$, cations for these studies. Transport of cations in NIPA-AA gels is compared with that of an uncharged electroactive probe 1,1'-ferrocenedimethanol, $Fc(MeOH)_2$, in solutions of various ionic strength. The aim of this work is to determine how the diffusion coefficients and the concentration of electroactive probes in thermoresponsive gels are effected by the ionic strength, composition of gels, and the discontinuous volume phase transition of NIPA-AA hydrogels.

EXPERIMENTAL SECTION

Materials. N-Isopropylacrylamide (NIPA, 97%), N, N'-methylenebisacrylamide (BIS, 99%), N, N, N', N'-tetramethylethylenediamine (TMED, redistilled), acrylic acid (AA), and ammonium persulfate (99.99+%) were purchased from Aldrich. High purity lithium perchlorate was purchased from Aldrich or Fluka. Hexaammineruthenium (III) chloride ($Ru(NH_3)_6Cl_3$) was from Alfa, and 1,1'-ferrocenedimethanol ($Fc(MeOH)_2$) was purchased from Fluka. Ferrocenylmethyltrimethylammonium iodide and ammoniumhexafluorophosphate were Strem chemicals. Ferrocenylmethyltrimethylammonium ($FcTMA^+$) hexafluorophosphate was synthesized by mixing aqueous solutions of ferrocenylmethyltrimethylammonium iodide and ammoniumhexafluorophosphate, and then by recrystallization from acetone-water solution. All materials were used as received except for AA, which was purified by vacuum distillation (21 mm Hg, 52 °C). All gels and solutions were prepared using high purity water (Milli-Q, Millipore).

Gel preparation. Preparation of NIPA-AA copolymers and preparation of NIPA-AA gels were described previously [15]. In this work, a known mass or volume of $FcTMA^+$, $Fc(MeOH)_2$, or $Ru(NH_3)_6^{3+}$ solutions with or without 0.1 M $LiClO_4$ as a supporting electrolyte was added to a sample of a dry NIPA-AA copolymer. After three days at room temperature, a gel was formed with a well-defined polymer-to-solvent ratio and a known concentration of an electroactive probe. These gels exhibit discontinuous reversible volume phase transition at 45 ± 2.5 °C, which was determined visually. At this temperature a two-phase system exists, and approximately 40% of a solution mass is expelled from a collapsed gel. The phase transition temperature appears to be constant for all compositions of gels studied in this work.

Voltammetry and Chronoamperometry. Staircase voltammetry and chronoamperometry were applied with a model 283 potentiostat (Perkin-Elmer, PARC) and controlled via a PC computer.

All experiments were carried out in a three-electrode system. A platinum wire and a silver/silver chloride electrode (Perkin-Elmer, PARC) were used as a counter and a reference electrode, respectively. Working microelectrodes were 10, 25, and 26 μm in diameter platinum disk electrodes (Project Ltd., Warsaw, Poland). The radius of microelectrodes was determined by optical inspection. Platinum microelectrodes were polished with diamond suspension (Buehler) on a wet pad, and their surface was inspected optically with a Nikon, Model Epiphot 200, inverted microscope for reflected light. All experiments were performed in a water-jacked glass cell (volume of approximately 5 mL). The temperature of the cell was controlled by a refrigerated circulator (Isotemp model 1016P, Fisher Scientific). The chronoamperometric experiments were conducted in a Faraday cage. The experimental parameters for chronoamperometry were: pulse time 20 s and sample frequency 50 Hz; 20 scans were collected for each temperature. The parameters for staircase voltammetry were: step height 3 mV and frequency 5 Hz. An average of current signals from at least 5 measurements was used to calculate the corresponding diffusion coefficient.

Viscosity Measurements. Gel viscosity measurements were performed using a Brookfield digital rheometer (model DV-III) with a LV spindle set. The revolution rate of the spindle was 1.5 rpm for less viscous gels and 0.1 or 0.2 rpm for more viscous gels. These measurements were performed at room temperature (24 ± 1°C). Solution viscosity measurements were performed using an Ostwald viscometer immersed in a temperature controlled water bath (24.0 ± 0.2 °C).

RESULTS AND DISCUSSION

Monocharged cationic probe, $FcTMA^+$

Steady-state voltammetry at a platinum disk microelectrode was used to study transport of $FcTMA^+$ in NIPA-AA gels of various compositions. Steady-state oxidation waves of $FcTMA^+$ were very well defined. The reproducibly of limiting currents in NIPA-AA gels was excellent, with relative standard deviation, *rsd*, not higher than 1.4% (calculated from 15 voltammograms). The shape of steady-state voltammograms of $FcTMA^+$ oxidation was almost identical in NIPA-AA gels with and without $LiClO_4$, in pure water without a gel, and in aqueous solutions with $LiClO_4$. However, reproducibility of the limiting currents was not as good in solutions as in gels, and *rsd* was 2.1% and 2.5% in 0.1 M $LiClO_4$ and pure water, respectively. This difference in reproducibility illustrates how the solid-like structure of the NIPA-AA gel protects the system against any distortions by convection.

The diffusion coefficient of a species in an ideal solution is described by Stokes-Einstein equation

$$D = kT/(6\pi\eta a) \tag{3}$$

where k is the Boltzmann constant, T is temperature, η is the viscosity of solution, and a is the radius of the diffusing species. According to this equation, diffusion coefficients are inversely proportional to the viscosity of an ideal solution. However, the diffusion coefficient of $FcTMA^+$ in the NIPA-AA gel cannot be predicted solely by the Stokes-Einstein relationship. Table 1 shows the dependence of the viscosity of a gel and the diffusion coefficient of $FcTMA^+$ on the concentration of a NIPA-AA copolymer in the gel. It also compares data for NIPA-AA gels with those for a solution. Note that those results are reported for swollen gels at temperatures below the discontinuous volume phase

transition. As one can see, a decrease of the diffusion coefficient of $FcTMA^+$ in gels is very small compare to changes of viscosity of the system. For example, the diffusion coefficient of $FcTMA^+$ in 4% NIPA-AA gel is only 25.6% smaller than that in aqueous solution, while the macroscopic viscosity of that gel is approximately six orders of magnitude greater than that of an aqueous solution. This shows that the macroscopic and microscopic viscosities of gels are significantly different, and that transport of $FcTMA^+$ in NIPA-AA gels at temperatures below the volume phase transition is controlled by the local microscopic viscosity of the system. A very similar situation has been observed for $Fc(MeOH)_2$ in NIPA-AA gels; the diffusion coefficient of $Fc(MeOH)_2$ in 4% NIPA-AA gel was 38% smaller than that in aqueous solution [15]. This very low resistance of diffusion of ionic probes on macroscopic viscosity of polymeric networks indicates the potential usefulness of these gels as semi-rigid electrolytes for electrochemical applications. A new model for description of the diffusion of small molecules in diluted polymeric gels has been proposed and tested for $Fc(MeOH)_2$ and TEMPO [8].

Figure 1 shows the dependence of the diffusion coefficient of $FcTMA^+$ on temperature of NIPA-AA hydrogels of various compositions and 0.1 M $LiClO_4$ solution. For temperatures below the volume phase transition of NIPA-AA gels, diffusion coefficients of $FcTMA^+$ increase with an increase of temperature, as predicted by Stokes-Einstein relation; these gels are in the swollen state. The temperature range of an increasing diffusion coefficient narrows for higher concentrations of a copolymer in a gel, and it is 5 – 45 °C and 5 – 25 °C for 1% to 4% NIPA-AA gels, respectively.

The experimental data for the temperature range from 5 °C to 25 °C presented in Figure 1 were analyzed in terms of an Arrhenius-like equation

$$D = Ae^{-Ea/RT} \qquad (4)$$

where D is the diffusion coefficient of a probe, A is the frequency factor, E_a is the activation energy of diffusion for that probe, R is the gas constant, and T is the absolute temperature. The activation energy of diffusion can be determined from the slope of the linear dependence of ln$D$ on $1/T$. Those experimentally determined dependencies were: $\ln D = -2258/T - 4.40$, $\ln D = -2298/T - 4.31$, $\ln D = -2313/T - 4.37$, $\ln D = -2194/T - 4.76$, and $\ln D = -2226/T - 4.73$ (D in cm^2s^{-1}, T in K) for 0.1 M $LiClO_4$ solution, 1%, 2%, 3%, and 4% NIPA-AA gels with 0.1 M $LiClO_4$, respectively, with the correlation coefficients higher than 0.999. The calculated values of activation energy of diffusion of $FcTMA^+$ in NIPA-AA hydrogels of various compositions are presented in Table 1. The E_a-values are 18.8 $kJmol^{-1}$ and 18.5 $kJmol^{-1}$ for 0.1 M $LiClO_4$ solution and 4% NIPA-AA gel with 0.1 M $LiClO_4$, respectively, and they are identical within experimental error. As one can see from Table 1, E_a-values for all gels and solutions do not differ. This confirms that the microscopic viscosity of solutions and swollen gels are very similar [30], and shows that the three-dimensional structure of polymeric gels is open for diffusion of small species.

When NIPA-AA gels undergo discontinues volume phase transition, two phases are formed, a collapsed gel phase, and an expelled solution phase. Transport of $FcTMA^+$ in collapsed NIPA-AA gels is very different from that in the swollen gel. As shown in Figure 1, the diffusion coefficient of $FcTMA^+$ decreases significantly as a result of the volume phase transition, and this decrease is more pronounced for larger concentrations of copolymer in the gel. For example, the diffusion coefficient of $FcTMA^+$ in 4% NIPA-AA gel at 50 °C determined from voltammetric experiments is 2.39×10^{-6} cm^2s^{-1}, only 20.6% of that in 0.1 M $LiClO_4$ solution (11.6×10^{-6} cm^2s^{-1}), while for 1% NIPA-AA gel at the same temperature the diffusion coefficient of $FcTMA^+$ is 9.57×10^{-6} cm^2s^{-1}, 82.5% of that in 0.1 M $LiClO_4$ solution. It should be pointed out here, that these diffusion coefficient values were determined from steady-state voltammetry according to eq. 1, with the assumption that the

concentration of $FcTMA^+$ in the gel does not change during the discontinuous volume phase transition.

To find out if our assumption was correct, and to determine diffusion coefficient of $FcTMA^+$ in collapsed NIPA-AA gels independent of concentration, we performed chronoamperometric experiments and determined diffusion coefficient of $FcTMA^+$ from eq. 2. The comparison of the temperature dependence of the diffusion coefficient of $FcTMA^+$ in 2% NIPA-AA gel from chronoamperometric and steady-state voltammetric results shows, that for temperature below the volume phase transition, the diffusion coefficient values obtained by both methods are very close. This means that the concentration of $FcTMA^+$ does not change with temperature for swollen gels. However, near and above the volume phase transition temperature, approximately 45 °C, the diffusion coefficients of $FcTMA^+$ determined from steady-state voltammetry are lower than those determined from normalized chronoamperometry. This effect can be seen even for lower temperature, approximately 30 °C, for 4% NIPA-AA gel. For example, the diffusion coefficients of $FcTMA^+$ in the collapsed NIPA-AA gels determined from normalized chronoamperometry at 55 °C were 9.6×10^{-6} cm^2s^{-1} and 5.3×10^{-6} cm^2s^{-1} for 2% and 4% gels, respectively, 1.34 and 2.94 of those determined from steady-state voltammetry, and 0.74 and 0.41 of those determined in 0.1 M $LiClO_4$ solution of the same temperature. The difference between diffusion coefficient values determined by steady-state voltammetry and chronoamperometry indicates the change in the concentration of $FcTMA^+$ in NIPA-AA gel near and above volume phase transition temperature. Now, concentration of $FcTMA^+$ in the gels can be calculated from the steady-state voltammetric current using values of D from chronoamperometry and eq. 1. Estimated concentration of $FcTMA^+$ remaining in the collapsed gel was 0.75 mM and 0.34 mM for 2% and 4% gels, respectively, which represents 75% and 34% of the original concentration of $FcTMA^+$. At 45 °C, the estimated concentration of $FcTMA^+$ remaining

in the collapsed gel was 0.96 mM and 0.48 mM for 2% and 4% gel, respectively. The larger the concentration of the copolymer in the gel, the larger decrease in the concentration of $FcTMA^+$ in the collapsed gel was observed, and with the increase of the temperature, the concentration of the probe in the collapsed gels decreased. As one can see the volume phase transition of NIPA-AA gels results in a decrease of the concentration of a cationic probe as well as its diffusion coefficient.

Since NIPA-AA gels are weakly negatively charged, attractive electrostatic interactions can be expected between negatively charged carboxylic moieties of NIPA-AA polymeric network and any cations in the system. Those interactions should be the strongest in systems of very low ionic strengths. A series of experiments has been performed in solutions and gels without added supporting electrolyte; the results are presented in Figure 2. As one can see, the transport coefficient of $FcTMA^+$ in pure water, calculated according to eq. 1, is slightly lower than that with electrolyte, with an average value of 0.885 of that in 0.1 M $LiClO_4$ solution. This is due to the migration of $FcTMA^+$; the direction is opposite to that of diffusion, and therefore, decreases the total flux and current of oxidation of $FcTMA^+$. According to theoretical predictions [31], the total steady-state current for 1-electron oxidation of a monocharged cation should be 0.849 of the purely diffusional current.

For temperatures below the volume phase transition of NIPA-AA gels, there is no difference between the diffusion coefficients of $FcTMA^+$ in 2% gel with and without 0.1 M $LiClO_4$; in both cases they increase with an increase of temperature. However, after the volume phase transition occurs, a decrease of the diffusion coefficient of $FcTMA^+$ in 2% gel without supporting electrolyte is more significant than that in 2% gel with 0.1 M $LiClO_4$. For example, at 55 °C the diffusion coefficient was 7.2×10^{-6} cm^2s^{-1} and 3.7×10^{-6} cm^2s^{-1} for 2% gels with and without electrolyte, respectively. The *D*-value in 2% gel without electrolyte is only 0.51 of that in 2% gel with

electrolyte. Diffusion coefficients obtained by chronoamperometry at the same temperature were 9.6×10^{-6} cm^2s^{-1} and 6.2×10^{-6} cm^2s^{-1} for 2% gels with and without electrolyte respectively; the *D*-value for the gel without electrolyte was 0.65 of that with electrolyte. This indicates that there are strong electrostatic attractive interactions between $FcTMA^+$ and the negatively charged polymeric network without electrolyte, and those interactions are much stronger than those with high concentration of $LiClO_4$. The estimated concentration of $FcTMA^+$ remaining in the collapsed gel without electrolyte was 0.61 mM, 61% of the original concentration.

In order to compare diffusivity of cations in NIPA-AA gels with diffusivity of neutral molecules, we studied the diffusion of $Fc(MeOH)_2$ as an electroactive probe. Voltammetric curves of the oxidation of $Fc(MeOH)_2$ were well defined and the limiting currents were reproducible, with *rsd* of 2.1%, 2.0%,1.9%, and 2.3% for 2% NIPA-AA gels with 0.1 M $LiClO_4$, 2% gels without electrolyte, 0.1 M $LiClO_4$ solution, and pure water, respectively. Diffusion coefficients of $Fc(MeOH)_2$ in various NIPA-AA gels in their swollen state are listed in Table 2. Only small difference, approximately 16%, is observed between diffusion coefficients of $Fc(MeOH)_2$ in solutions and NIPA-AA gels. This behavior has been reported previously for swollen gels [8,15], and an appropriate model for the description of transport of small molecules in polymeric gels has been proposed [8]. No difference can be seen between systems with and without electrolyte; since $Fc(MeOH)_2$ is an uncharged probe, there are no electrostatic interactions between the gel network and the uncharged electroactive probe.

Trivalent cationic probe, $Ru(NH_3)_6^{+3}$

Voltammetric and chronoamperometric experiments were performed for a trivalent positively charged probe, hexaaminеruthenium (III) cation, $Ru(NH_3)_6^{+3}$, in NIPA-AA gels in their swollen state and during volume phase transitions. The one-electron reduction of $Ru(NH_3)_6^{+3}$ at Pt microelectrodes

results in a very well defined voltammetric wave. The reproducibly of limiting currents was excellent, with *rsd* (calculated from 15 voltammograms) of 0.48%, 0.70%, 0.77% and 0.87% in 2% NIPA-AA gel with 0.1 M NaCl, 2% gel without electrolyte, 0.1 M NaCl solution, and water, respectively. Diffusion coefficients of $Ru(NH_3)_6^{+3}$ in solutions and in NIPA-AA gels were calculated according to eq. 1, and their dependence on temperature in 0.1 M NaCl solution and NIPA-AA gels with 0.1 M NaCl is presented in Figure 3. As expected for a simple solution, the diffusion coefficient of $Ru(NH_3)_6^{+3}$ increases with an increase of temperature in 0.1 M NaCl solution. However, in NIPA-AA gels with 0.1 M NaCl it increases with temperature before the phase transition occurs, and than decreases at temperatures close to the volume phase transition and above. For NIPA-AA gels in their swollen state, diffusion coefficients of $Ru(NH_3)_6^{3+}$ are only slightly lower than those in an aqueous solution. For example, at 25 °C (see Table 3) the diffusion coefficient of $Ru(NH_3)_6^{3+}$ in 4% gel with 0.1 M NaCl is only 26.7% smaller than that in 0.1 M NaCl solution. This behavior is very similar to that of monocharged cation, $FcTMA^+$. The activation energies of diffusion, E_a, of $Ru(NH_3)_6^{3+}$ were calculated using the Arrhenius-like equation, eq. 4, and are presented in Table 3. Similarly to $FcTMA^+$ and $Fc(MeOH)_2$ [8,15], there are no significant differences in E_a-values for the probe ions between gels and an aqueous solution.

As one can see from Figure 3, the diffusion coefficient of $Ru(NH_3)_6^{3+}$ in NIPA-AA gels decreases significantly after the volume phase transition occurs, and this effect is more pronounced than that for $FcTMA^+$ (compare with Figure 1). This difference is probably due to electrostatic interactions of multicharged cations with the polymeric network in its collapsed state.

Apparently, there is a significant difference in interactions of NIPA-AA polymeric network with molecules of a solvent, and other species present in the system for gels in their swollen and collapsed state. Tokuhiro [32] has determined the number and distribution of water molecules in

swollen NIPA gels by measuring the densities of those gels using a specially designed pycnometer. His measurements verified the earlier findings that the physical state of water in gels is not identical to that of the liquid water [32]. For ionic NIPA gels modified with acrylic acid groups, he found that acrylic acid residues could retain water molecules more than 9 times that of NIPA residues. It might be that these bound water molecules hinder interactions of probe cations with acrylic acid groups of swollen NIPA-AA gels. However, with increasing temperature, the hydrogen bonds between water molecules, and water molecules and polymer networks will gradually be destroyed because of vigorous thermal motions of water molecules. This leads to a loss of water molecules that are loosely bound to the polymer network. It induces a decrease in the total volume of the polymeric gel and brings various chemical groups of NIPA network closer to each other [32]. For NIPA-AA gels, negative acrylic groups are much closer to each other in collapsed gels than in the swollen state and as a result the total charge density of NIPA-AA collapsed gel is much higher than that of a swollen network. Since $Ru(NH_3)_6^{3+}$ is a trivalent cation, it should be strongly attracted by negative acrylic groups. As a consequence, the diffusion movement of $Ru(NH_3)_6^{3+}$ is slowed down by such interactions, and its diffusion coefficient in collapsed gels decreases more than that of $FcTMA^+$.

Figure 4 presents results obtained by chronoamperometry, according to eq. 2. As one can see, the diffusion coefficient of $Ru(NH_3)_6^{3+}$ decreases when the temperature reaches the volume phase transition. However, it does not decrease as significantly as indicated by steady-state voltammetry (compare with Figure 3). For example, at 45 °C the concentration of $Ru(NH_3)_6^{3+}$ remaining in a collapsed gel was 3.6 mM and 1.2 mM, 90% and 30% of the original probe concentration for 2% and 4% gel, respectively. At 55 °C, that concentration was 2.7 mM and 0.64 mM only 68% and 16% of the original $Ru(NH_3)_6^{3+}$ concentration for 2% and 4% gel, respectively. From the comparison of results for $FcTMA^+$ and $Ru(NH_3)_6^{3+}$, one can see that $Ru(NH_3)_6^{3+}$ is excluded more effectively from

the collapsed gel than $FcTMA^+$. It has been demonstrated that NIPA gels in the collapsed state strongly adsorbed the organic molecule (e.g., benzoic acid) dissolved in water [33] while NIPA-SSNa gels exclude salts (e.g., LiCl, CH_3COONa, KSCN) from their collapsed state above the transition temperature [27]. Since $Ru(NH_3)_6Cl_3$ is an inorganic salt it may be excluded more effectively from the collapsed NIPA-AA gel.

To study electrostatic interactions between the $Ru(NH_3)_6^+$ probe and the polymeric network, 2% NIPA-AA gel without electrolyte was prepared. Figure 5 shows the temperature dependence of the transport of $Ru(NH_3)_6^+$ in water and 2% NIPA-AA gel without supporting electrolyte, and for comparison in 0.1 M NaCl solution and 2% gel with 0.1 M NaCl. The transport coefficients of $Ru(NH_3)_6^{+3}$, calculated according to eq. 1, are higher in pure water than those in 0.1 M NaCl solution. This is due to migration contributing to the total flux of $Ru(NH_3)_6^{3+}$ in solution without electrolyte, and consequently higher limiting current compared to purely diffusion current. According to theoretical prediction [31], the total limiting current for one electron reduction of +3 charged ion should be 1.173 of the diffusion current. Our experimental value is 1.19, and it is very closed to that theoretically expected.

For temperatures lower than 25 °C, well below volume phase transition temperature, there is no difference in the transport coefficients of $Ru(NH_3)_6^{3+}$ in 2% gel without electrolyte and those in 2% gel with 0.1 M NaCl. Transport of $Ru(NH_3)_6^{3+}$ in the gel without electrolyte begins to slow down above 25 °C, and this effect is more significant at higher temperatures. For example, transport coefficient in 2% gel without electrolyte, calculated from eq. 1, is 42% and 12% of that in pure water at 35 °C and 55 °C, respectively, and 56% and 24% of that in 2% gel with 0.1 M NaCl at 35 °C and 55 °C, respectively. At 55 °C the transport coefficient of $Ru(NH_3)_6^{3+}$ in 2% collapsed NIPA-AA gel without electrolyte determined by chronoamperometry is 5.8×10^{-6} cm^2s^{-1}, only 35% of that in water

without polymeric network (we assume the same ionic strength of both media), and the calculated concentration of $Ru(NH_3)_6^{3+}$ remaining in the collapsed gel without electrolyte was 0.82 mM, only 21% of the original concentration of the probe (slightly higher than 16% for a collapsed gel with NaCl). Note that for monovalent cation, $FcTMA^+$, the transport coefficient in 2% NIPA-AA gel without electrolyte was 58% of that in water, and for an uncharged probe, $Fc(MeOH)_2$, it was 76% of that in water under the same conditions determined by chronoamperometry. As one can see, the transport coefficient of the trivalent cationic probe in collapsed gels without electrolyte decreases more significantly than that of the monocharged cationic probe, and the transport of cations is significantly slower than that of uncharged probes. The concentration of the trivalent cationic probe remaining in completely collapsed gels without electrolyte is much smaller than that of monocharged cationic probe.

Summary

We have used two methods, steady-state voltammetry and normalized chronoamperometry to study the transport phenomena in thermoresponsive NIPA-AA hydrogels during their volume phase transitions. Two positive charged probes, $FcTMA^+$ and $Ru(NH_3)_6^{3+}$, and one uncharged probe, $Fc(MeOH)_2$, were used in our experiments. Although the macroscopic viscosity of NIPA-AA gels was approximately six orders of magnitude greater than that of an aqueous solution, there was no significant difference in transport behavior of various probes in those gels in their swollen state. The activation energy of diffusion, E_a, for the cationic probes was the same in swollen gels and in aqueous solutions. This indicates that the local microscopic viscosity of swollen NIPA-AA gels is almost identical to that of an aqueous solution. Since NIPA-AA gels are weakly negatively charged, electrostatic interactions were expected between polymeric network and cationic species in those systems. However, no significant electroattractive interactions were detected in swollen NIPA-AA

gels before the volume phase transition. Both electroanalytical techniques, steady-state voltammetry and normalized chronoamperometry, gave very similar results for the diffusion behavior of electrochemical probes in swollen NIPA-AA gels.

After the volume phase transition occurs, diffusion coefficients of cationic probes decrease significantly, and this effect is more pronounced for multicharged probes than monocharged species. Since the total volume of the polymeric network decreases, and as a consequence the distance between ionic moieties of the polymer decreases, the charge density of the polymer increases. This change of the charge density of the gel results in modification of electrostatic interaction between polymeric units, between polymeric units and water, and also between polymeric units and cations in the gel. The electro-attractive force between the negatively charged AA groups in the NIPA-AA network and cationic probes becomes stronger thus hinder the diffusion movement of the cationic probes. This effect depends on the ionic strength of the system. In NIPA-AA gels without supporting electrolyte, cationic probes become strongly attracted to negatively charged acrylic groups, and therefore, their transport in collapsed gels is significantly slower than in systems with excess electrolyte.

The volume phase transition of NIPA-AA gels results in a change of the concentration of ionic probes in the gel phase. The concentration of cationic probes remaining in the completely collapsed gel phase becomes lower than the original concentration in the swollen gel. This decrease in concentration depends on the composition of the gel; it is more significant for higher percentages of NIPA-AA polymer in the gel, and it depends on the ionic strength of the systems, changes are more pronounced in gels without electrolyte than in those of high ionic strength.

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Table 1. Diffusion Coefficient and Activation Energy of Diffusion of $FcTMA^+$, and Viscosity of NIPA-AA Gels.

Medium [a]	D ($cm^2\ s^{-1}$) @ 25 °C	E_a ($kJ\ mol^{-1}$)	η (cP) @ 24 °C
0.1 M $LiClO_4$ solution	6.3×10^{-6}	18.8	9.4×10^{-1}
1% NIPA-AA gel	5.5×10^{-6}	19.1	2.0×10^{4}
2% NIPA-AA gel	5.4×10^{-6}	19.2	2.0×10^{5}
3% NIPA-AA gel	4.8×10^{-6}	18.2	2.4×10^{6}
4% NIPA-AA gel	4.7×10^{-6}	18.5	5.6×10^{6}

[a] All gels prepared with 0.1 M $LiClO_4$

Table 2. Diffusion Coefficient of $Fc(MeOH)_2$ and Viscosity of NIPA-AA Gels.

Medium [a]	D ($cm^2 s^{-1}$) @ 25 °C	η (cP) @ 24 °C
0.1 M $LiClO_4$ solution	6.3×10^{-6}	9.4×10^{-1}
1% NIPA-AA gel	5.2×10^{-6}	2.0×10^{4}
2% NIPA-AA gel	4.3×10^{-6}	2.0×10^{5}
3% NIPA-AA gel	3.6×10^{-6}	2.4×10^{6}
4% NIPA-AA gel	3.9×10^{-6}	5.6×10^{6}

[a] All gels prepared with 0.1 M $LiClO_4$

Table 3. Diffusion Coefficient and Activation Energy of Diffusion of $Ru(NH_3)_6^{3+}$, and Viscosity of NIPA-AA Gels.

Medium [a]	D (cm^2s^{-1}) @ 25 °C	E_a (kJ mol^{-1})	η (cP) @ 24 °C
0.1 M $LiClO_4$ solution	7.9×10^{-6}	14.8	9.4×10^{-1}
1%NIPA-AA gel	7.1×10^{-6}	16.1	2.0×10^{4}
2%NIPA-AA gel	6.3×10^{-6}	15.6	2.0×10^{5}
3%NIPA-AA gel	6.3×10^{-6}	16.0	2.4×10^{6}
4%NIPA-AA gel	5.8×10^{-6}	16.5	5.6×10^{6}

[a] All gels prepared with 0.1 M NaCl

FIGURE CAPTIONS

Figure 1. Temperature dependence of the diffusion coefficient of $FcTMA^+$ determined by steady-state voltammetry in: (▲) 0.1 M $LiClO_4$ solution, (◆) 1%, (●) 2%, (■) 3%, and (▼) 4% NIPA-AA gel; 1 mM $FcTMA^+$, all gels with 0.1 M $LiClO_4$.

Figure 2. Temperature dependence of the diffusion coefficient of $FcTMA^+$ determined by steady-state voltammetry in: (▲) 0.1 M $LiClO_4$ solution, (Δ) water, (●) 2% NIPA-AA gel with 0.1 M $LiClO_4$, and (O) 2% NIPA-AA gel without electrolyte.

Figure 3. Temperature dependence of the diffusion coefficient of $Ru(NH_3)_6^{3+}$ determined by steady-state voltammetry in: (▲) 0.1 M NaCl solution, (◆) 1%, (●) 2%, (■) 3%, and (▼) 4% NIPA-AA gel; 4 mM $Ru(NH_3)_6^{3+}$, all gels with 0.1 M NaCl.

Figure 4. Temperature dependence of the diffusion coefficient of $Ru(NH_3)_6^{3+}$ determined by chronoamperometry in: (▲) 0.1 M NaCl solution, (◆) 1%, (●) 2%, (■) 3%, and (▼) 4% NIPA-AA gel; 4 mM $Ru(NH_3)_6^{3+}$, all gels with 0.1 M NaCl.

Figure 5. Temperature dependence of the diffusion coefficient of $Ru(NH_3)_6^{3+}$ determined by steady-state voltammetry in: (▲) 0.1 M NaCl solution, (Δ) water, (●) 2% gel with 0.1 M NaCl, and (O) 2% NIPA-AA gel without electrolyte.

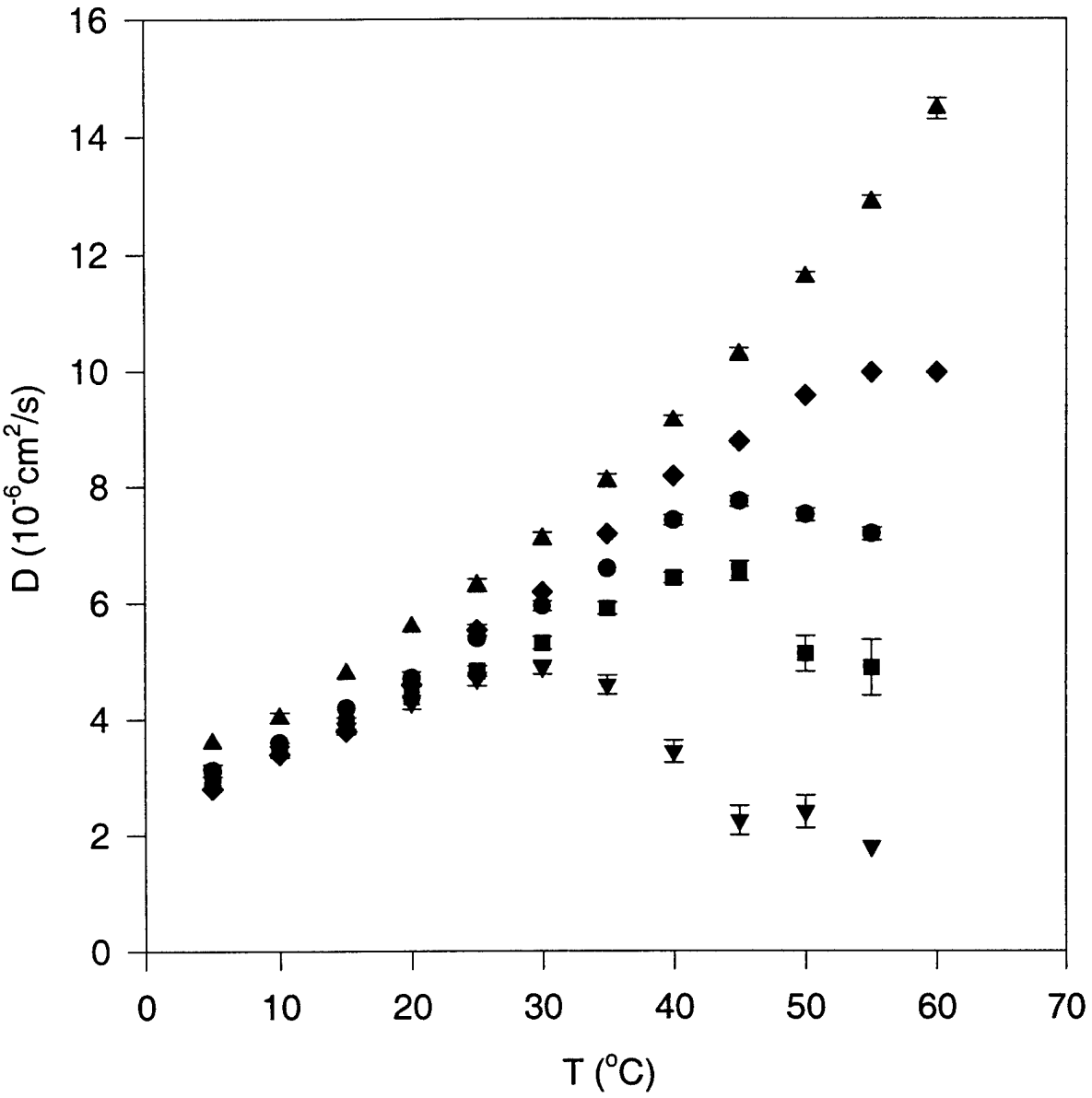

Figure 1

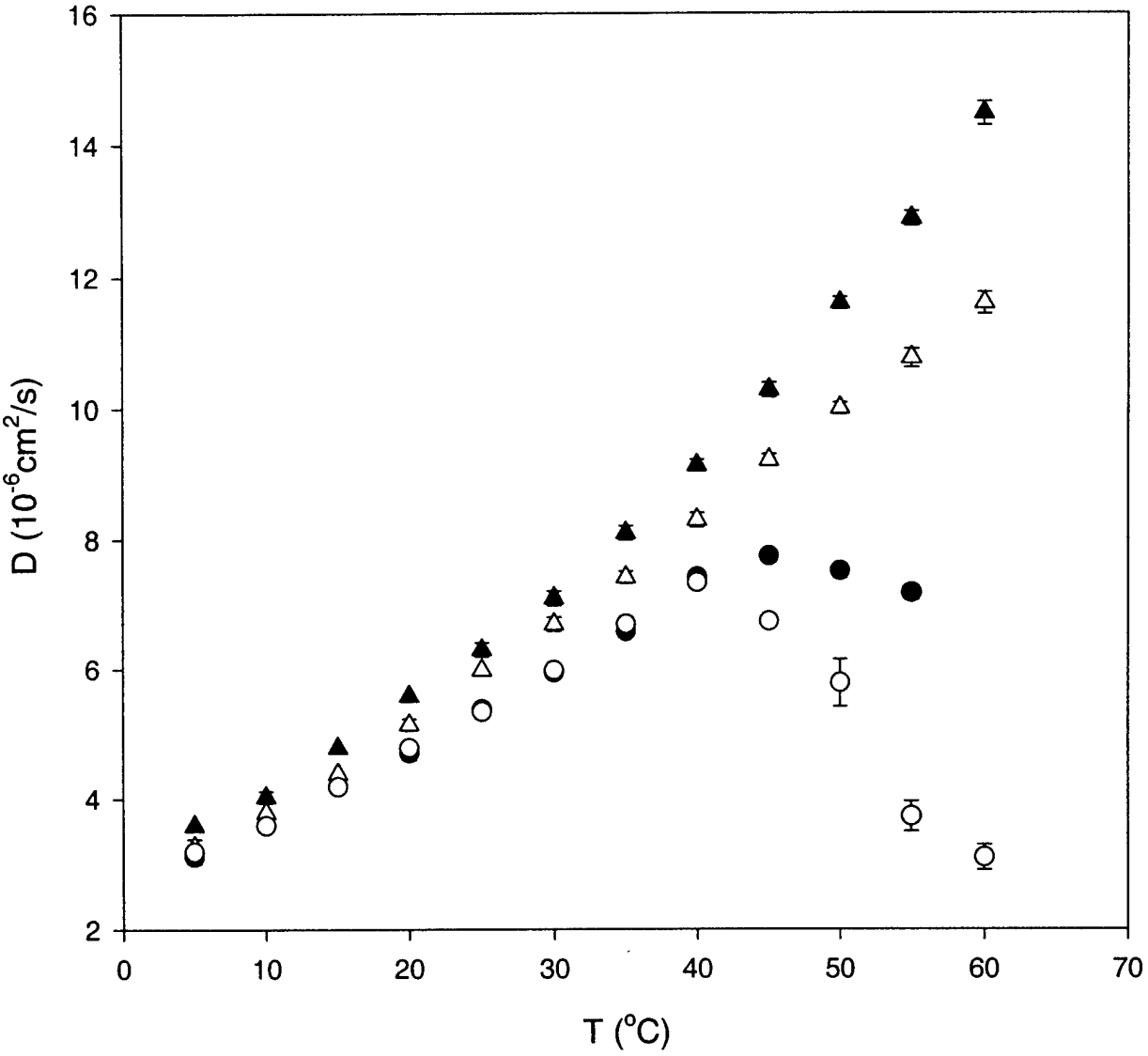

Figure 2

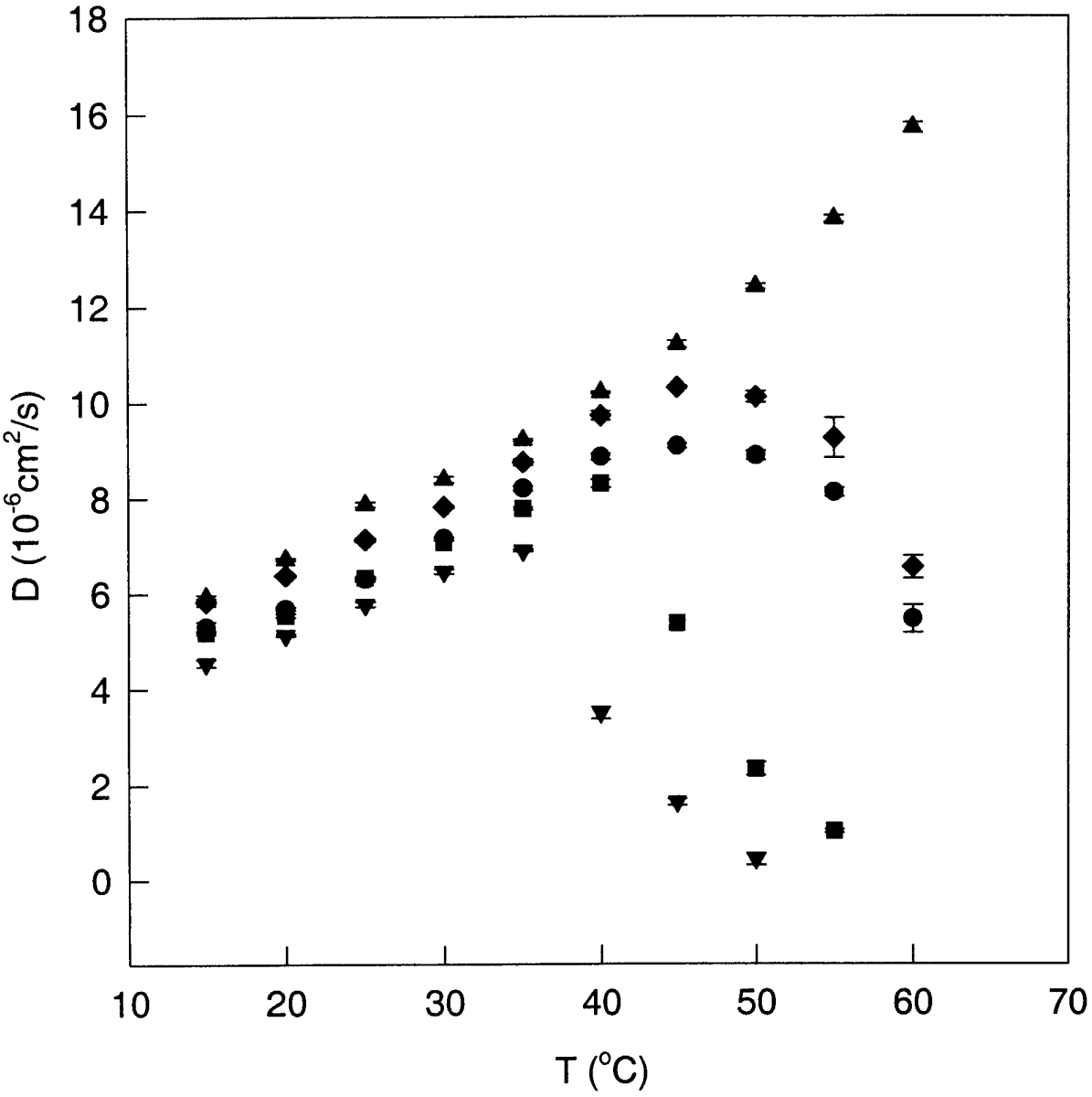

Figure 3

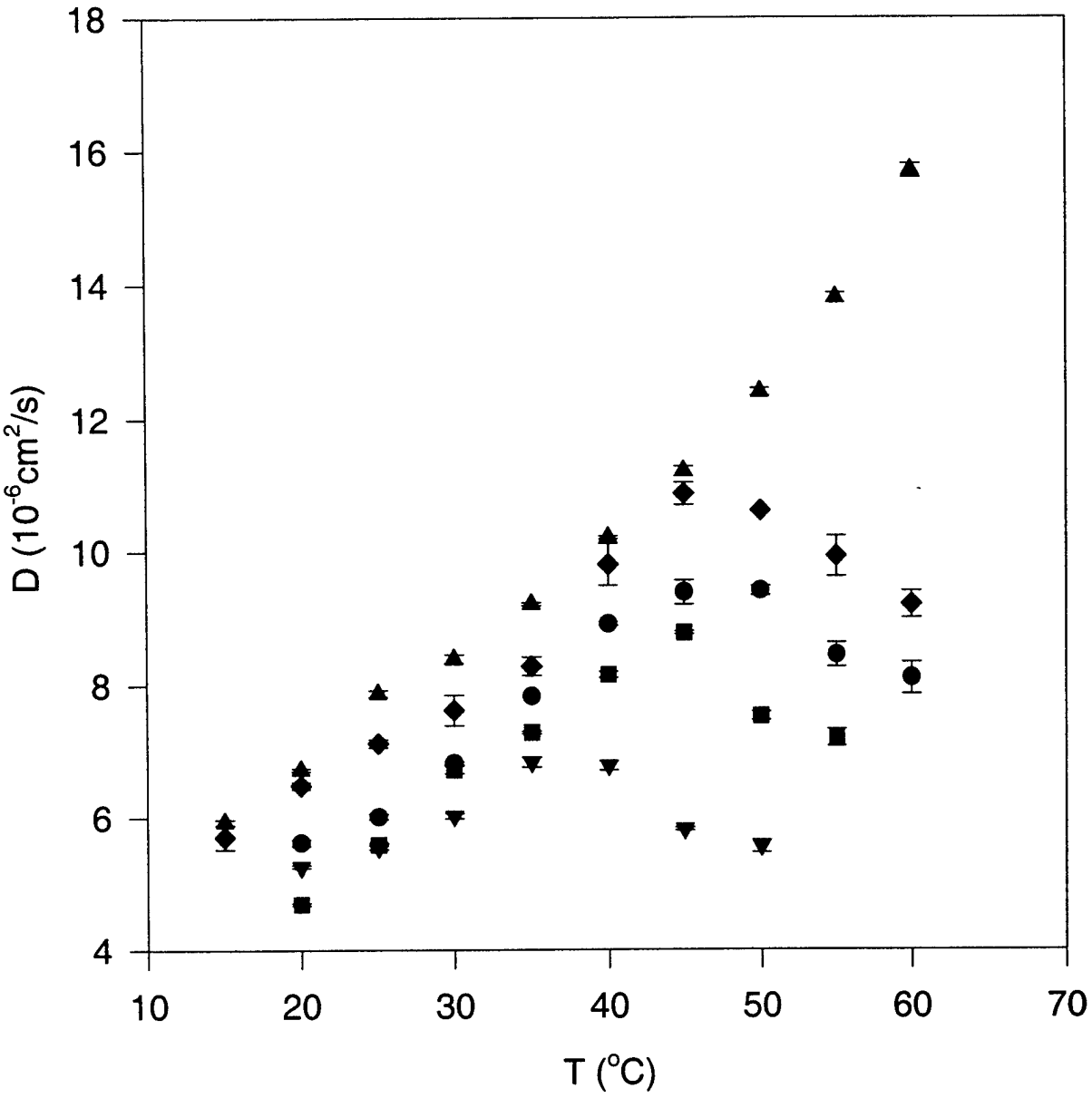

Figure 4

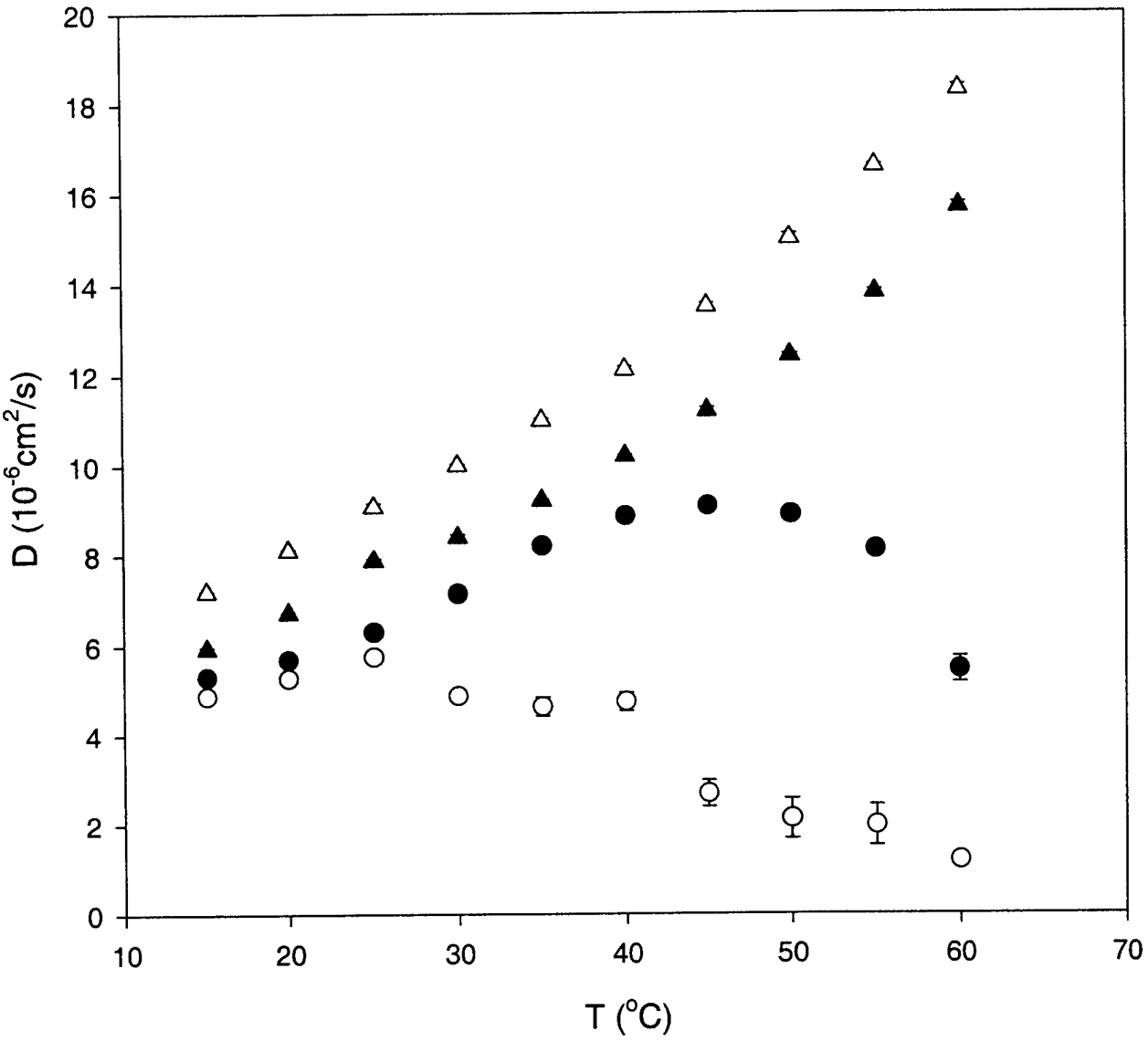

Figure 5